

Superabsorbent Hydrogel of Acrylic Acid/Potassium Acrylate Copolymers by Ultraviolet Photopolymerization: Synthesis and Properties

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ABSTRACT: Synthesis of superabsorbent hydrogel (SAHG) of acrylic acid-potassium acrylate copolymer by direct Ultraviolet (UV) photopolymerization is a new method. The effects of degree of neutralization of acrylic acid (AA), photoinitiators, crosslinking agents, and exposure time of UV light on water absorbent properties were investigated. The results showed that the water absorbency (*Q*) and the salt solution (NaCl, 0.9%) absorbency (*Q_s*) of SAHG, based on Irgacure 651, are high, reaching about 1400 and 130 mL/g, respectively. UV absorption spectrum proved that peak of UV absorption of Irgacure 651 matched the UV light source we used. Among the crosslinking agents, *N,N'*-methylene bisacrylamide is more efficient than others, because of its very small content and high *Q*. ¹³C NMR spectrometry was used to identify the mechanism of

crosslinking reaction through esterification of hydroxyethyl acrylate (HEA) and 2-hydroxypropyl acrylate (HPA) with carboxylic acid group in acrylic acid-ammonium acrylate copolymerization, but efficiency of crosslinking reaction by esterification was lower than that of copolymerization of vinyl group in crosslinking agent. The *Q* of acrylic acid-potassium acrylate copolymer of SAHG reaches 1592 mL/g under the following conditions: degree of neutralization of acrylic acid is 80%, content of Irgacure 651 is 0.25 wt %, content of HEA is 0.2 wt %, and exposure time is 10 min. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1181–1187, 2006

Key words: superabsorbent hydrogel; UV photopolymerization; copolymer; acrylic acid; crosslinking agent

INTRODUCTION

Hydrogels are crosslinked polymer networks that swell in water but do not dissolve in it. Superabsorbent hydrogel (SAHG) is an important kind of functional polymer, which is widely used in many fields, such as in amelioration of agricultural soils, sanitation stuffs, timbering, etc. SAHG is capable of absorbing hundreds or even thousand times of water as much as its own weight, and is capable of high water retention under pressure. The traditional method of synthesis of SAHG is thermal polymerization, including solution polymerization and inverse suspension polymerization.^{1–16} When compared with thermal polymerization, ultraviolet (UV) photopolymerization has many merits, such as polymerization at room temperature, simple technology including very short exposure time and successional production, and less pollution.¹⁷ In this study, we propose a route of UV photopolymerization to synthesize acrylic acid-potassium acrylate

copolymer SAHG, and then the influence of the degree of neutralization of acrylic acid (AA) by aqueous potassium hydroxide of the SAHG is discussed. The effects of photoinitiators, crosslinking agents, and exposure time on the properties of AA-potassium acrylate copolymer SAHG were also investigated.

EXPERIMENTAL

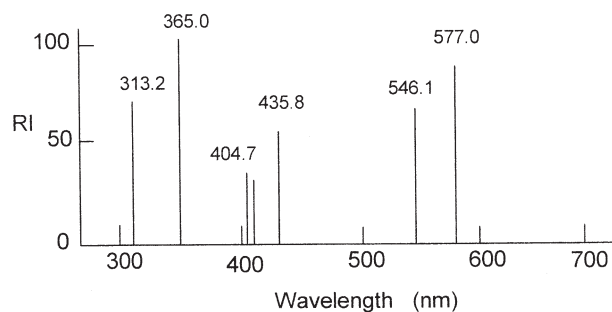
Materials

Acrylic acid (AA), hydroxyethyl acrylate (HEA), and 2-hydroxypropyl acrylate (HPA) were purchased from Beijing Dongfang Chemical Factory. Potassium hydroxide and *N,N'*-methylene bisacrylamide were purchased from Beijing Chemical Factory. Irgacure 651, Irgacure 184, Irgacure 819, Darocur 1173, and Irgacure 2959 were provided by Ciba-Geigy Company.

Instrument

UV light (high pressure mercury light, wavelength distribution is shown in Scheme 1, the main wavelength of radiation is about 365 nm), 700 W, *I* =

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Scheme 1 Wavelength distribution of UV light.

1.1 mJ/cm²; UV-260 UV-visible-spectrophotometer; BRUKER-AV300 nuclear magnetic resonance spectrometer. The SAHG of AA-potassium acrylate copolymer were dried and ground into powder for analyzing by ¹³C nuclear magnetic resonance spectrometry.

Synthesis

AA was first neutralized by aqueous potassium hydroxide to a certain degree of neutralization (40–95%), followed by the addition of photoinitiators (Irgacure 651, Irgacure 184, Irgacure 819, Darocur 1173, or Irgacure 2959) and crosslinking agents (*N,N'*-methylene bisacrylamide, HEA, or HPA) and it was mixed. Subsequently it was exposed under 700 W UV light for a certain interval of time. The SAHG of AA-potassium acrylate copolymer was obtained, which was dried and ground into particles of certain size for further characterization.

Characterization

Water absorbency (Q , ml/g) and salt solution (NaCl, 0.9%) absorbency (Q_s , ml/g) were determined by the natural filtration method¹⁸. SAHG (0.1 g) sample was taken in a filtration bag, the bag was then submerged into 500 mL of water (100 mL salt solution) for 10 min, the Q (Q_s) is calculated by the ratio of the volume of loss water (salt solution) to the mass of SAHG. The diameter of each sides of SAHG sample is about 0.07–0.08 cm, crosslinking ratio ($G\%$) (Percentage of insoluble part of SAHG, the molecule of it was crosslinked, G was calculated by the mass ratio of $M_1:M_2$ (M_1 : mass of SAHG extracted by distilled water; M_2 : mass of the SAHG) was determined by the natural filtration method.¹⁸ (The diameter of each sides of SAHG sample is about 0.07–0.08 cm)

Double bond content (wt.%) was analyzed by iodometry,¹⁹ which was expressed in the content of AA in samples.

RESULTS AND DISCUSSION

Degree of neutralization

AA was first neutralized by aqueous potassium hydroxide to give a mixture of AA and acrylate potas-

sium monomers before the UV photopolymerization. Figure 1 shows the effects of different degree of neutralization on water absorbent characteristics of the SAHG. Q increased as the degree of neutralization increased from 40 to 80%, the top Q can reach 805 mL/g. When the degree of neutralization increases from 80 to 95%, the Q of SAHG tends to decrease. This is due to two factors determining the capacity of water absorption of SAHG, one is the content of hydrophilic groups (carboxylic group) in the polymer, and another is osmotic pressure between SAHG and water. So the Q of SAHG is determined by the joint effect of these two factors. Higher the degree of neutralization of SAHG, greater the content of potassium salt inside the SAHG, which causes the osmotic pressure to raise and Q to increase. But with the increasing degree of neutralization, the content of carboxylic group in SAHG decreases, which lowers the Q . The appropriate degree of neutralization of AA-potassium acrylate copolymer SAHG is 80%. In this case, the effects of content of hydrophilic group factor and osmotic pressure factor are at a proper point and the Q is highest at 805 mL/g. Because of the same reason, Q_s of SAHG also follows such a rule. When the degree of neutralization reaches 80%, highest Q_s of 89 mL/g is obtained. The degree of neutralization should be controlled around 80% can we get high water absorbent characteristics of SAHG.

Photoinitiators

Effects of photoinitiator and exposure time

The influencing factors of photoinitiator play a very important role in the UV photopolymerization of SAHG.²⁰ Scheme 2 lists the molecular formulas of the

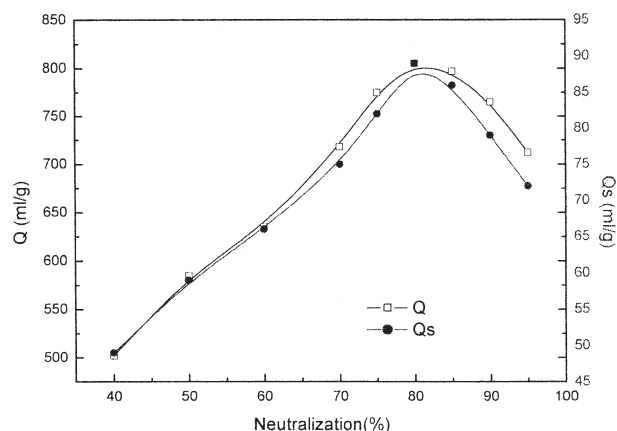
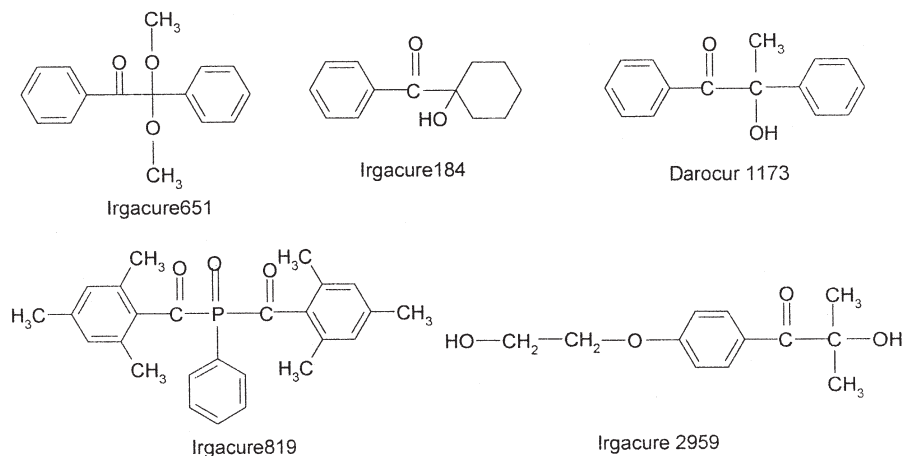


Figure 1 Effects of the degree of neutralization on the Q and Q_s of SAHG photoinitiator, Irgacure 651 (0.15 g/mol AA-potassium acrylate monomers); crosslinking agent, *N,N'*-methylene bisacrylic amide (0.005 g/mol AA-potassium acrylate monomers); monomer content, 55%; exposure time, 10 min.



Scheme 2 Molecular formula of photoinitiators.

photoinitiators that we used. As shown in Table I, there are five photoinitiators (Irgacure 651, Irgacure 184, Irgacure 819, Darocur 1173, or Irgacure 2959) used in synthesizing AA-potassium acrylate copolymer SAHG. The conditions of photopolymerization are shown in Table I. The content of photoinitiator (crosslinking agent) of the SAHG is calculated by ratio of mass of photoinitiator (crosslinking agent) to mass

of AA and acrylate monomers. From Table I, we learn that longer the exposure time, higher the Q , the higher G and the lesser double bond in SAHG. Excessive exposure leads to tiny degradation of crosslinked copolymer of SAHG. Exposure time longer than 20 min causes a decrease in Q and G of SAHG. From Table I, we can also see that the appropriate exposure time of SAHG is about 10–20 min, and Irgacure 651 is the

TABLE I
Effects of Photoinitiators and Exposure Time on SAHG

Photoinitiator type	Exposure time (min)	Q (mL/g)	G (%)	Double bond content (wt %)
Irgacure 184	1	101	38.5	4.12
	5	175	86.9	0.95
	10	315	92.8	0.43
	20	356	93.1	0.32
	30	345	93.0	0.36
Irgacure 651	1	253	67.6	0.93
	5	492	92.2	0.31
	10	515	93.8	0.18
	20	506	94.2	0.16
	30	496	93.8	0.16
Irgacure 819	1	135	41.1	3.17
	5	156	59.9	1.15
	10	327	67.8	0.47
	20	467	90.5	0.31
	30	452	90.1	0.33
Darocur 1173	1	96	33.8	5.39
	5	172	62.2	1.29
	10	285	83.1	0.58
	20	335	90.5	0.33
	30	328	90.2	0.35
Irgacure 2959	1	109	40.9	3.02
	5	312	87.6	0.65
	10	375	91.3	0.32
	20	362	91.7	0.30
	30	355	90.1	0.35

Photoinitiator content, 0.15 wt %; crosslinking agent, *N,N'*-methylene bisacrylamide (0.025 wt %); degree of neutralization, 80%; exposure time, 10 min.

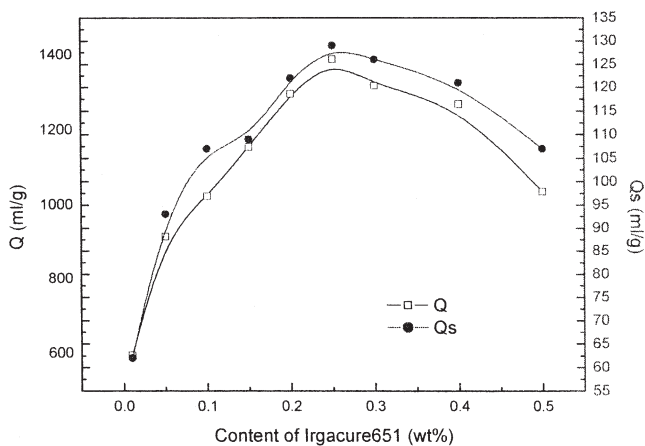
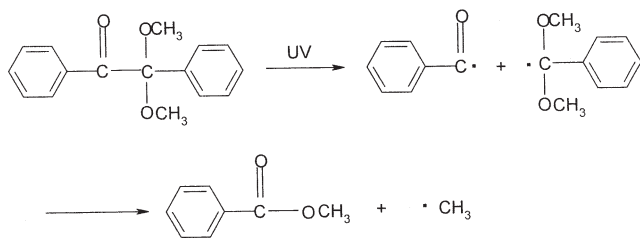


Figure 2 Effect of content of photoinitiators on the Q of SAR, degree of neutralization, 80%; exposure time, 10 min; crosslinking agent, N,N' -methylene bisacrylamide (0.0015 wt %).

most efficient photoinitiator to initiate photopolymerization when compared with other photoinitiators for its short exposure time, getting high G and low double bond content.

Effects of content of photoinitiator

Figure 2 shows the effects of content of photoinitiator, Irgacure 651, on Q and Q_s of SAHG. As the content of Irgacure 651 increases, Q and Q_s increases significantly. When the content of Irgacure 651 reaches 0.25%, the top values of Q and Q_s are 1388 and 129 mL/g respectively. Scheme 3 shows the processes of photoinitiation fragmentation under UV light of Irgacure 651, including the chemical structure and photolysis mechanism of the photoinitiators and the resultant radicals, so the photopolymerization processes belonged to radical polymerization by nature. Irgacure 651 is able to release methyl radical under UV irradiation, and methyl radical has small volume and high ability of diffusion, and for this reason Irgacure 651 has high activity of initiation than other photoinitiators in Table I. Figure 3 shows the UV spectra of the photoinitiator Irgacure 651. Distinct UV absorption peaks appear between 320 and 400 nm for this photo-



Scheme 3 Processes of fragmentation of Irgacure 651.

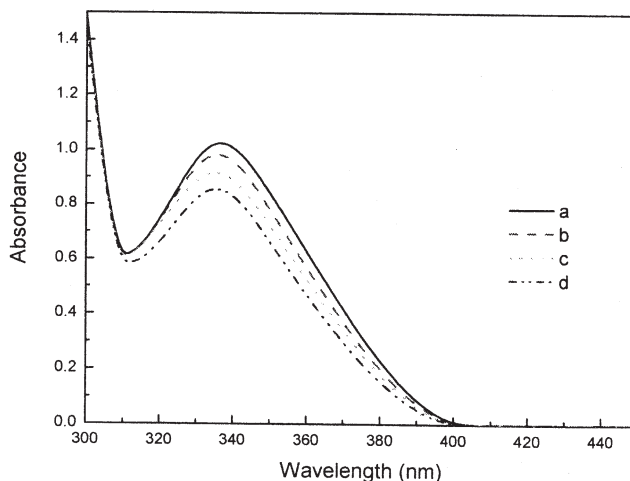
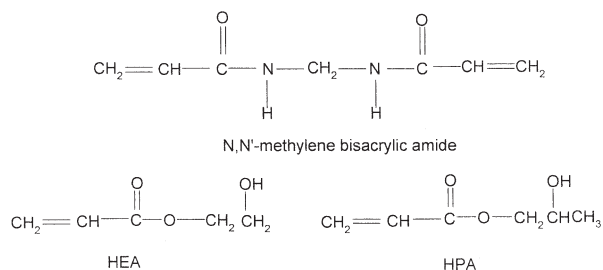


Figure 3 UV absorption spectra of Irgacure 651, solvent, ethyl alcohol; concentration of Irgacure 651, 0.001 g/mL; exposure time, a 0 s, b 10 s, c 30 s, and d 60 s.

initiator. With the increasing of exposure time (0, 10, 30, and 60 s) of Irgacure 651, the height of UV absorption peaks of these three photoinitiators decrease clearly. It means that the more the exposure time, the more the fragmentation of photoinitiator and the irradiation wavelength of the UV light that we used conforms to the UV absorption wavelength of Irgacure 651. The main irradiation wavelength of the UV light is 365 nm.

Crosslinking agents

Scheme 4 shows the molecular structure of the crosslinking agents that were used for this study. As a crucial effective factor, crosslinking agents directly determine the water absorption characteristics and mechanical properties of AA-potassium acrylate SAHG. During the process of copolymerization of AA and acrylate potassium monomers, the crosslinking reactions may be performed by copolymerization and esterification. In this paper, different kinds of crosslinking agents: N,N' -methylene bisacrylamide, HEA, HPA are used separately.



Scheme 4 Molecular structure of crosslinking agents.

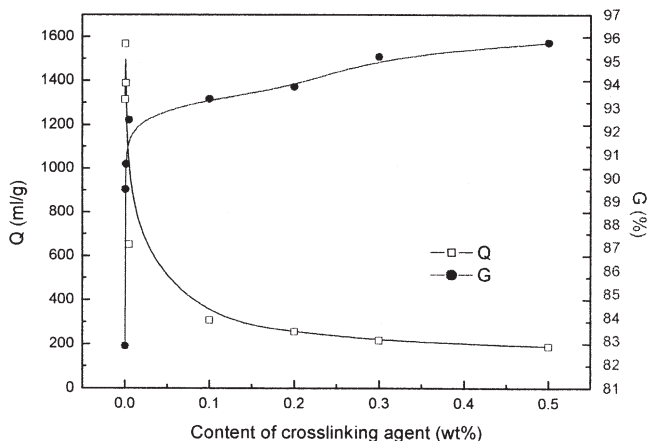


Figure 4 Effects of crosslinking agent (*N,N'*-methylene bisacrylamide) content on *Q* and *G* of AA-potassium acrylate SAHG, degree of neutralization, 80%; photoinitiator, Irgacure 651 (0.25 wt %); exposure time, 10 min.

Figure 4 shows, when using *N,N'*-methylene bisacrylamide as crosslinking agent, the peak value of *Q* of SAHG is 1568 mL/g, and the respective content of the crosslinking agent is 0.001%. The *G* of the SAHG increases as the content of *N,N'*-methylene bisacrylamide increases. From Figures 5 and 6 we can see that the content of HEA and HPA are about 0.2%, the peak value of *Q* of SAGH are 1592 and 1125 mL/g, respectively. It is no doubt that *N,N'*-methylene bisacrylamide is the most efficient crosslinking agent among the three, because of its very small amount resulting in higher *Q* and *G* of SAHG. Using HEA as a crosslinking agent, high *Q* of 1568 mL/g for SAHG can be obtained.

From Figures 4, 5, and 6 we also acquired the consequence that the content of HEA and HPA in the SAHG are much higher than that of *N,N'*-methylene

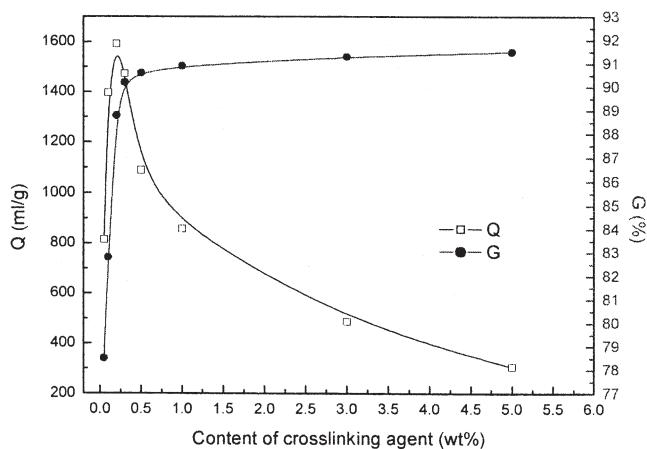


Figure 5 Effects of crosslinking agent (HEA) content on *Q* and *G* of AA-potassium acrylate SAHG, degree of neutralization, 80%; photoinitiator, Irgacure 651 (0.25 wt %); exposure time, 10 min.

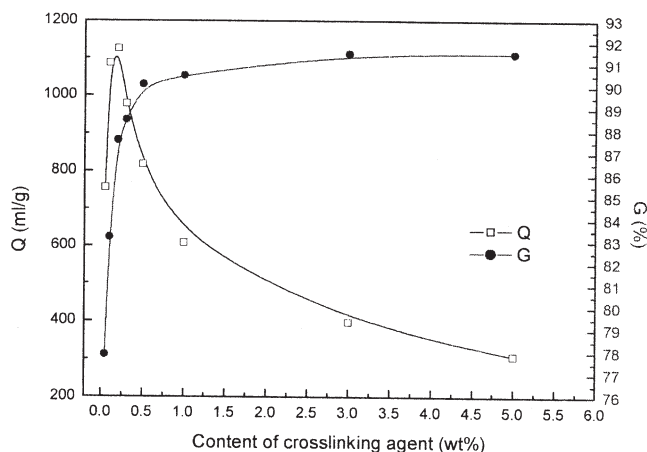
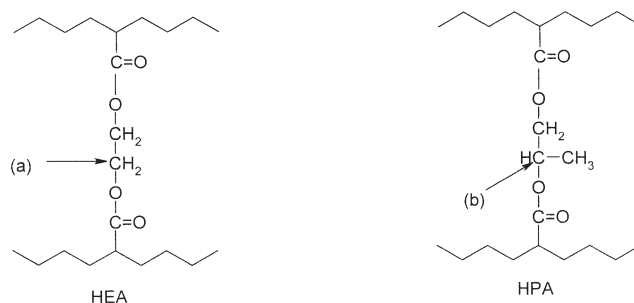
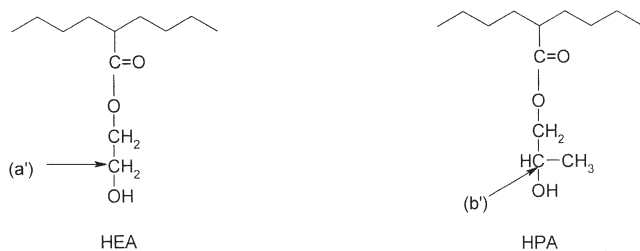


Figure 6 Effects of crosslinking agent (I-IPA) content on *Q* and *G* of AA-potassium acrylate SAHG, degree of neutralization, 80%; photoinitiator, Irgacure651 (0.25 wt %); exposure time, 10 min.

bisacrylamide to reach higher *Q*. The reason to explain is that, the crosslinking mechanisms of these three kinds of crosslinking agents are different. The crosslinking reaction of *N,N'*-methylene bisacrylamide is the two double bonds of its molecular structure copolymerizing with the double bonds of AA and acrylate potassium of SAHG. But in the case of HEA and HPA, the crosslinking mechanism include both copolymerization reaction and esterification reaction, for there were one double bond and one hydroxyl group in molecular structure, and hydroxyl group can esterified partly with carboxyl group at main chain of AA-potassium acrylate copolymer. When copolymerization of the SAHG proceeded, on one hand HEA or HPA copolymerized with AA and acrylate potassium, on the other hand a part of hydroxyl group in HEA or HPA esterified with carboxyl group of AA, which had already copolymerized into main chains of AA-potassium acrylate copolymer of SAHG. But in this water solution circumstances, the reaction degree of crosslinking mechanism of esterification is lower than that of copolymerization, which means the efficiency



Scheme 5 Crosslinking structure of HEA and HPA in SAHG.



Scheme 6 Uncrosslinking structure of HEA and HPA in SAHG.

of crosslinking by copolymerization is much higher than that of crosslinking by esterification. So HEA or HPA must be added in excess to the polymerization system than that of *N,N'*-methylene bisacrylamide to get good water absorption characteristics of SAHG.

Scheme 5 shows the crosslinking structure of HEA and HPA in AA-potassium acrylate copolymer of SAHG, and the C δ of C (a) and C (b) are 62.7 and 66.9 ppm, respectively. Scheme 6 shows that if there is no esterification crosslinking reaction of HEA or HPA with carboxyl group of AA in copolymerization system of SAHG, the C δ of C (a') and C (b') are 59.7 and 62.9 ppm, respectively.²¹ Figure 7 shows the ¹³C NMR spectrometry of HEA, and from Figure 7 we can see that near C δ 62.8256 ppm there is a clear peak. Similarly for HPA shown in Figure 8, distinct peak appears near C δ 67.0231 ppm. This means that the

mechanism of crosslinking reaction of HEA and HPA occurs through esterification, as mentioned previously is correct.

CONCLUSIONS

Synthesis of AA-potassium acrylate copolymer SAHG by UV photopolymerization is a new method. The proper degree of neutralization of AA by potassium hydroxide for reaching higher water absorbency of SAHG is 80%. Irgacure 651 is a kind of high efficient photoinitiator that initiate AA and acrylate potassium monomers to copolymerize. Using Irgacure 651 as photoinitiator and an exposure time of 5–10 min, good properties of SAHG were obtained, such as short exposure time but high *Q*, *G*, and low double bond content. *N,N'*-methylene bisacrylamide and HEA were high efficient crosslinking agents for synthesizing SAHG with good water absorption capacity. Copolymerization and esterification are two main mechanisms of crosslinking HEA and HPA with AA and acrylate potassium monomers in synthesizing SAHG. AA-potassium acrylate SAHG with *Q* as high as 1592 mL/g has been attained by UV photopolymerization under the following conditions: degree of neutralization, 80%, Irgacure 651 (0.25 wt %) as photoinitiator, HEA (0.2 wt %) as crosslinking agent, and an exposure time of 10 min.

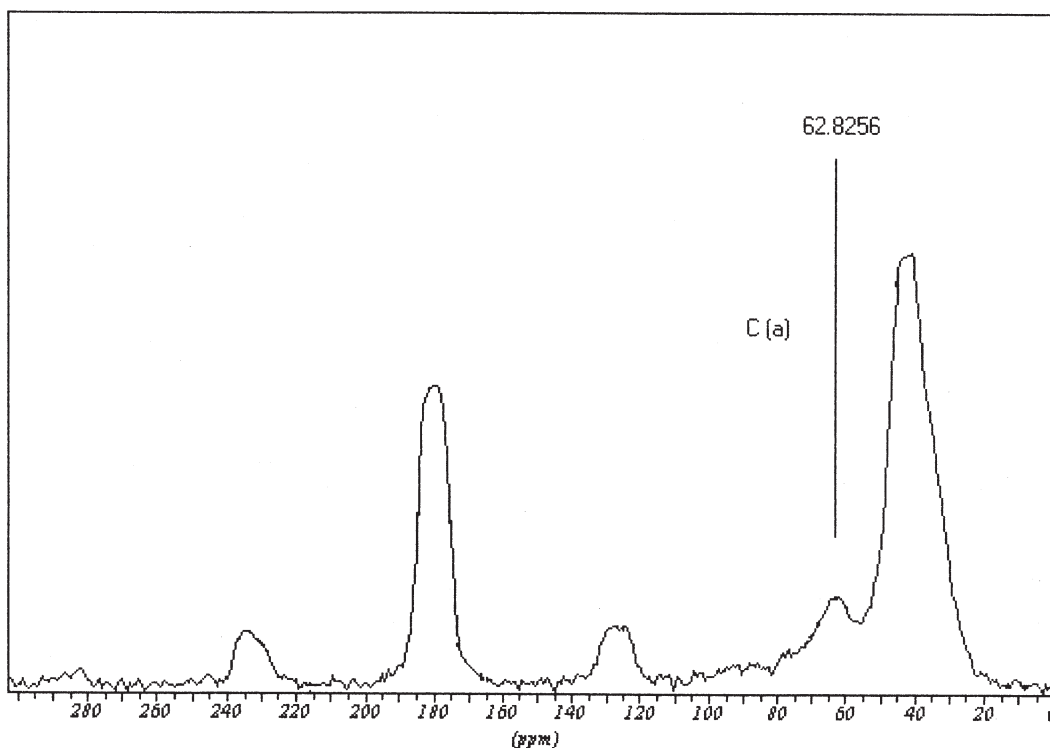


Figure 7 ¹³C NMR spectrometry of SAHG, crosslinking agent: HEA, 15 wt %.

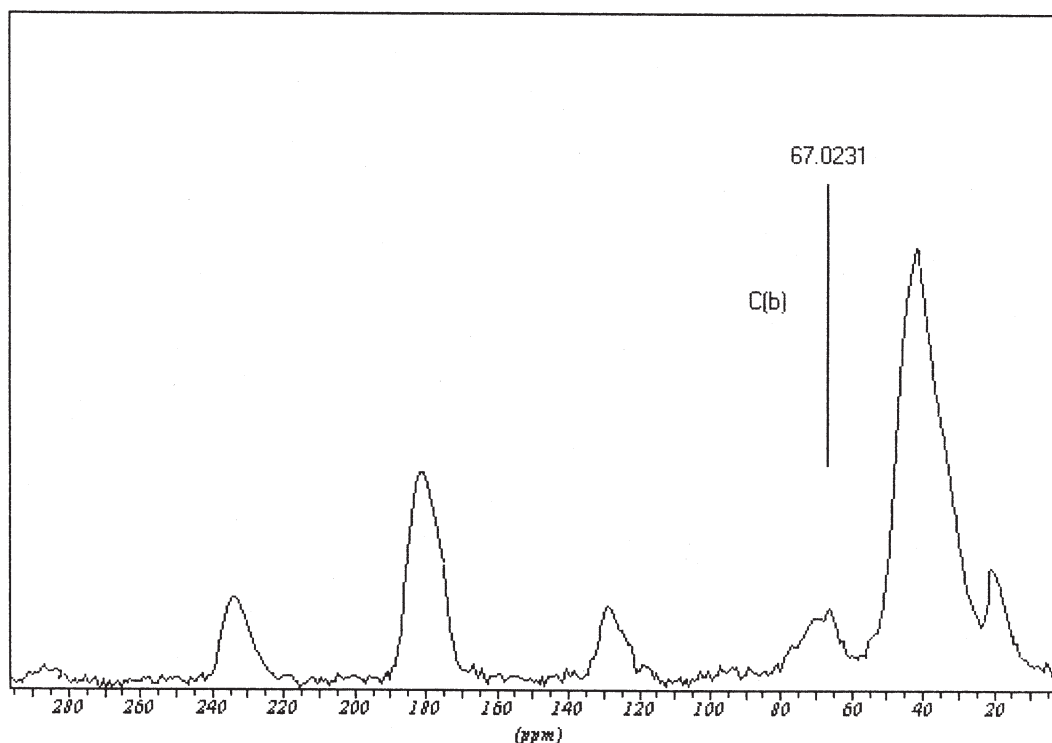


Figure 8 ^{13}C NMR spectrometry of SAHG, crosslinking agent: HPA, 15 wt %.

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